

PCT/PTO 28 JUN 2000

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

192784US2PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

39/505 264

INTERNATIONAL APPLICATION NO.

PCT/EP99/01821

INTERNATIONAL FILING DATE

18 FEBRUARY 1999

PRIORITY DATE CLAIMED

04 JUNE 1998

TITLE OF INVENTION

PROCESS FOR THE DETERMINATION OF MTBE IN THE GROUND AND AIR

APPLICANT(S) FOR DO/EO/US

Lucio DE ANGELIS

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2)).
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report
Notice of Priority
PCT/IB/308

U.S. APPLICATION NUMBER 09/581264

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

PCT/EP99/01821

192784US2PCT

20. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☒ Search Report has been prepared by the EPO or JPO **\$840.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) **\$670.00**
- ☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) **\$760.00**
- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$970.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) **\$96.00**

CALCULATIONS PTO USE ONLY**ENTER APPROPRIATE BASIC FEE AMOUNT =****\$840.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	4 - 20 =	0	x \$18.00	\$0.00
Independent claims	2 - 3 =	0	x \$78.00	\$0.00
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00

TOTAL OF ABOVE CALCULATIONS =**\$840.00**

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐

\$0.00**SUBTOTAL =****\$840.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

\$0.00**TOTAL NATIONAL FEE =****\$840.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐

\$0.00**TOTAL FEES ENCLOSED =****\$840.00**

Amount to be:
refunded \$
charged \$

- ☒ A check in the amount of **\$840.00** to cover the above fees is enclosed.
- ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**22850**

703-413-3000

Surinder Sachar
Registration No. 34,423

SIGNATURE

Marvin J. Spivak

NAME

24,913

REGISTRATION NUMBER

DATE

June 28, 2000

09/581264

PROCESS FOR THE DETERMINATION OF MTBE IN THE GROUND AND
AIR.

The present invention relates to a process for the determination of pollution by methyl ter butyl ether.

- 5 Methyl ter butyl ether (MTBE) is the most widely used among oxygenated additives for motor vehicles. Its addition improves combustion and significantly reduces the emission of carbon monoxide, especially during low winter temperatures. The possibility of a
- 10 leakage in the earth of fuels contained in underground tanks of service stations is probable. As a result of this, MTBE has been the object of a great deal of research with respect to its destiny in the environment and its potential impact on public health, mainly
- 15 bearing in mind that this substance is extremely volatile and soluble in water. In addition, if present, it remains in deep water and sediments as owing to its very limited biodegradability, with an odour that can be noticed starting from concentrations at a level of

20 ppb. Its cancerogenous activity, if existing, seems to be small.

There are various methods for determining and measuring MTBE: they range from gas chromatography to
5 IRA and flame-ionization, but they are all difficult to apply to the ground.

We have now overcome these problems by means of a process which allows the continuous monitoring of MTBE, in the ground and on the surface, using sensors in the
10 solid state.

In accordance with this, the present invention relates to a process for monitoring methyl ter butyl ether (MTBE) vapours, in concentrations equal to or higher than 0.1 ppm, in the ground and overlying
15 atmosphere comprising:

a) adopting a series of MTBE vapour sensors of which at least one in the earth, equipped with a membrane permeable to gases and impermeable to water, and at least one in the air on the surface of the ground,
20 these sensors consisting of

- a sensitive element made of a semi-conductor metal oxide containing platinum;
- a heater capable of bringing the temperature of said sensitive element to a range of 300 and 500°C;

25 b) - continuously observing the resistance variations

of the sensitive elements by interaction with MTBE,
- comparing the signals emitted by the sensor in the
earth and the sensor in the air on the ground-surface;
- evaluating on the basis of this comparison the
5 presence and concentration of MTBE in the surface
layers or depths of the ground and in the atmosphere
above the ground itself.

A further object of the present invention relates
to the device for effecting the process.

10 A typical embodiment of the invention is described
hereunder, with reference to figures 1 and 2 in which
equal numbers correspond to equal elements.

Figure 1 illustrates a sensor, in enlarged form.
The sensitive element 1 is produced by placing by
15 . screen printing, on an aluminum slab with dimen-
sions of 3 x 9 x 0.25 mm, a 40 micron layer of a tin
oxide paste, containing platinum. Powders are used
having a particle size of less than 1 micron containing
from 20 to 30% by weight of alumina and organometallic
20 platinum as catalyst in a quantity ranging from 0.1 to
1% by weight. A resistor (consisting of a layer of any
commercial screen printing conductor paste capable of
resisting at least 400°C) is deposited, again by
screen printing, on the opposite side of the slab,
25 to keep the sensitive element at an operating tempera-

ture of 300-500°C. After depositing the electric contacts also by screen printing, the slab is subjected to a baking step in an oven at 800-1000°C for an hour.

5 Finally the device, which forms the sensitive element, is assembled on a T078 2 container and inserted in a steel cylinder 3 closed by means of a flame-shield net 4. If the sensor described is fixed into the ground, a membrane 5, permeable to gases and imperme-
10 able to water, is inserted under the flame-shield net to prevent any possible water present in the earth from entering into contact with the sensitive element. An appropriate porous septum or even better a membrane made of ePTFE material can be used for the purpose.

15 The sensitive elements can alternatively be produced with other types of semi-conductor metal oxides, but still using platinum as catalyst.

The sensors are equipped with feeders, or alternatively batteries, to supply energy to the heater and
20 resistivity measurement circuit of the sensitive element.

Figure 2 illustrates an underground tank 6 of a service station for leadless fuels with a configuration with three sensors for the embodiment of the present
25 invention. Two sensors 7, like those described with a

gas permeable membrane, are fixed in the ground at the sides of the tank, a sensor 8 without a membrane inserted in the chamber 9 above the tank. 10 illustrates the data acquisition switchboard.

5 Sensors such as those described above have a sensitivity which is such as to signal the presence of vapours of gasoline containing MTBE or MTBE alone with concentrations even less than 1 ppm in the air. The possibility of comparing the signals coming from the
10 sensors fixed in the ground with those situated in the chamber above the tank over a period of time, make it possible to distinguish between leakages on the ground surface and losses from the underground tank.

In another embodiment of the same invention,
15 sensors can be placed along an underground pipe around it and on the ground surface above. In this case the signals emitted from the sensors can be sent via radio to a central unit for collection and processing.

A few examples are provided below for a better
20 understanding of the present invention but should not be considered as limiting the scope of the invention itself.

EXAMPLE 1

Using a sensor according to the one described
25 above, and a tin container, conductivity measurements

are carried out in the presence of gasoline vapours to which 10% of MTBE has been added.

In figure 3.(a) the trace shows the kinetics response of the sensor in relation to the time at various concentrations of gasoline.

Figure 3.(b) shows the variation in the resistance in relation to the concentrations of gasoline. As can be seen the response is proportional to the concentration logarithm and allows concentrations of less than 1 ppm to be detected.

EXAMPLE 2

With the procedure described above, a system consisting of two MTBE sensors and an electronic control unit is prepared.

One of the sensors, protected by an ePFTE membrane, is inserted, up to a depth of about 10 cm, in a tank of 50 x 40 x 30 cm full of sandy earth. The second sensor is placed at about 20 cm from the first and about 5 cm from the surface.

After a stabilization period of about 30 minutes 1 ml of gasoline containing 10% of MTBE is injected with a syringe into the ground, at a distance of 10 cm from the underground sensor and at a depth of 10 cm. In figure 4 the temporal point of the injection is indicated with the arrow A. As can be observed, the trace

registered by the sensor in the air (2) indicates an almost immediate decrease in resistance, whereas the trace registered by the sensor in the ground (1) indicates a delay of about 5 min. before the decrease
5 in resistance.

After a few hours, 1 ml of gasoline (indicated with the arrow B in figure 4B) is injected again. As can be observed, the trace of the sensor in the ground (1) begins to indicate a decrease in resistance start-
10 ing from the level reached with the previous injection of gasoline. This shows that the sensor is capable of monitoring a further leakage also starting from ground which has already been polluted.

With respect to the trace in air, this starts from
15 a much higher resistance value of the sensor as gasoline vapours dilute very rapidly in air, unlike the ground where the vapours interstitial tend to remain trapped.

The time delay of a few minutes in this case, shown by the response of the sensor fixed in the ground
20 with respect to that in the air depends on the fact that in the earth interstitial vapours of gasoline and MTBE, although being mobile enough to allow this type of measurement, need a certain amount of time to spread from the leakage point to the sensor. In air the
25 vapours obviously spread at a much faster rate and the

sensor consequently does not show significant delays.

As mentioned in the description, the different
behaviour of sensors in the ground and in the air
enables a leakage in the surface to be distinguished
5 from a leakage in depth in the ground.

CLAIMS

1. A process for determining methyl ter butyl ether (MTBE) vapours, in concentrations equal to or higher than 0.1 ppm, in the ground and overlying atmosphere comprising:
- 5 a) adopting a series of MTBE vapour sensors of which at least one in the earth, equipped with a membrane permeable to gases and impermeable to water, and at least one in the air on the surface
- 10 of the ground, these sensors consisting of
- a sensitive element made of a semi-conductor metal oxide containing platinum;
 - a heater capable of bringing the temperature of said sensitive element to a range of 300 and
- 15 500°C;
- b) - continuously observing the resistance variations of the sensitive elements by interaction with MTBE,
- comparing the signals emitted by the sensor in
- 20 the earth and the sensor in the air on the ground-surface;
- evaluating on the basis of this comparison the presence and concentration of MTBE in the surface layers or depths of the ground and in the atmo-
- 25 sphere above the ground itself.

2. The process according to claim 1, characterized in that the sensitive element is produced with tin oxide.
3. A device for determining methyl ter butyl ether (MTBE) vapours comprising:
- 5 a) a series of sensors of MTBE vapours consisting of a sensitive element produced with
- a 40 micron layer of semiconductor metal oxide containing 1% by weight of platinum,
 - 10 - a heater capable of bringing the temperature of said sensitive element to a range of 300 to 500°C,
- at least one of said sensors being equipped with a membrane permeable to gases and impermeable to
- 15 water for the protection of said sensitive element;
- b) an electronic evaluation system capable of
- continuously recording the variations in resistance of the sensitive elements by
 - 20 interaction with MTBE,
 - comparing the signals emitted by the sensor in the ground and the sensor in the air on the surface of the ground,
 - evaluating on the basis of this comparison
 - 25 the presence and concentration of MTBE in the

surface layers or depths of the ground and in the atmosphere above the ground itself.

4. The device according to claim 3, characterized in that the semiconductor metal oxide is tin oxide.

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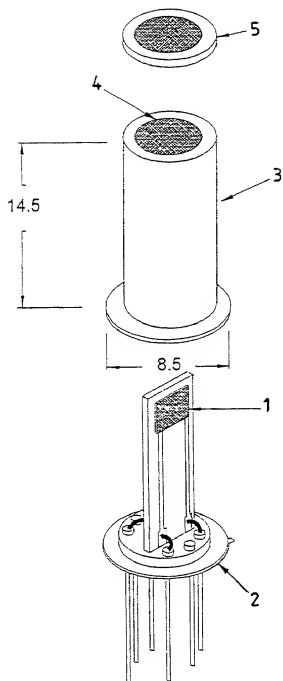
Fig.1

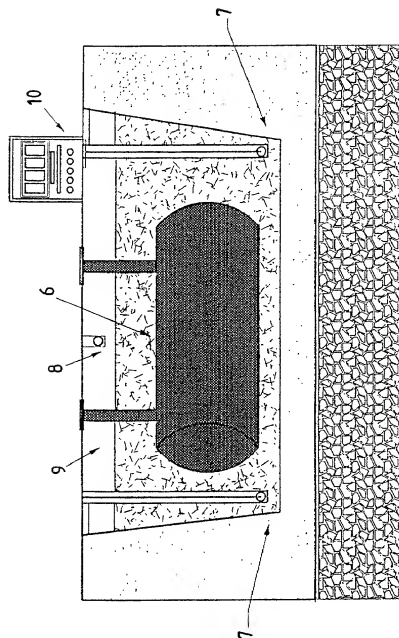
Fig.2

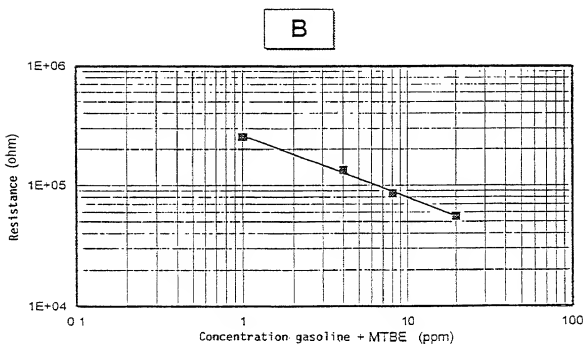
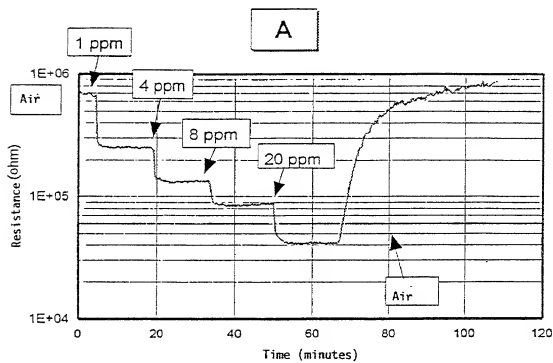
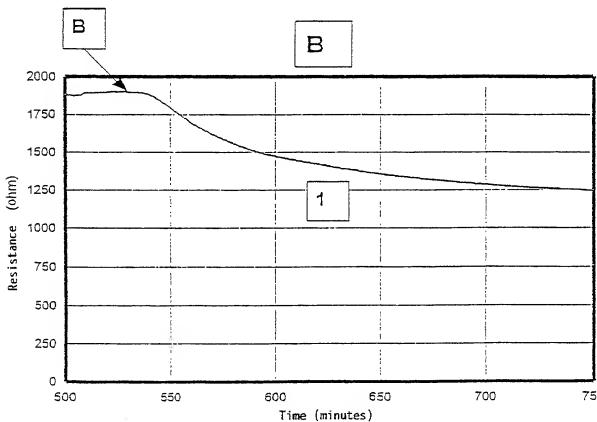
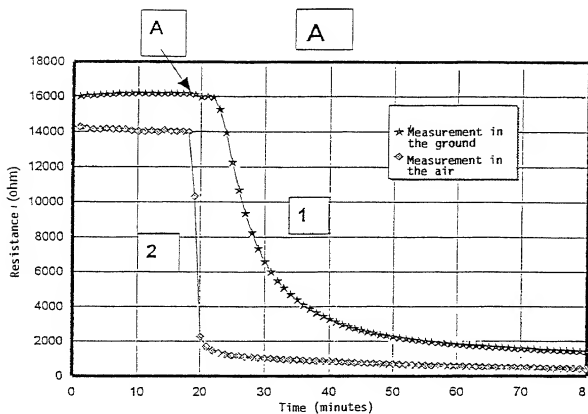
Fig.3

Fig.4

Declaration, Power Of Attorney and Petition

Page 1 of 3

WE (I) the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR THE DETERMINATION OF MTBE IN THE GROUND AND AIR

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number PCT/EP99/01821

on 18 FEBRUARY 1999,

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
MI98A001248	ITALY	4 JUNE 1998	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,
abandoned)

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	30

And we (I) hereby appoint: Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,752; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,820; Robert T. Pous, Reg. No. 29,092; Charles L. Gholz, Reg. No. 26,395; Vincent J. Sunderdick, Reg. No. 29,004; William E. Beaumont, Reg. No. 30,996; Robert F. Gnuse, Reg. No. 27,295; Jean-Paul Lavalleye, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Martin M. Zoltick, Reg. No. 35,745; Robert W. Hahl, Reg. No. 33,893; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Christina M. Gadiano, Reg. No. 37,628; Jeffrey B. McIntyre, Reg. No. 36,867; and Paul E. Rauch, Reg. No. 38,591; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C., whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1-co
NAME OF FIRST SOLE INVENTOR

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Citizen of: ITALY

Post Office Address:

same as above

30 MAY 2000

Date